

CLAY MINERALS OF THE SOUTHERN GREAT HUNGARIAN PLAIN

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INTRODUCTION

Core samples from two boreholes of "Makó—Hódmezővásárhely trench" were studied. This area extends on the southern part of the Great Hungarian Plain. Samples of Makó-1 and Makó-2 drillings represent the sedimentary sequences of the internal part of this Neogene basin having a relatively deep structural position [MUCSI, 1973].

The results of present paper give informations on the clay mineral content of formations of the Upper and Lower Pannonian substages and that of the Miocene epoch.

The Upper and Lower Pannonian according to the Hungarian classification correspond about to the Lower and Middle Pliocene, but the border between the Upper and Lower Pannonian does not coincide with that of the Middle and Lower Pliocene. The ages of the Miocene samples are Middle and Upper Miocene.

The border of the Upper and Lower Pannonian is at the depth of about 2300 m in the area investigated. The border between the Lower Pannonian and Miocene may be at 4156—4162 m.

The Makó-1 drilling ends in the Lower Pannonian substage, the Makó-2 went through the Neogene sequences and reached the bottom of the basin.

METHODS

After having been removed the amounts of carbonates and organic matter mica, montmorillonite, chlorite, kaolinite, quartz, feldspar and amorphous material were determined by chemical methods in the fraction of $10\ \mu$ of core samples.

ALEXIADES and JACKSON [1965] summarize the method as follows. The mica content was based on 8,29% K (10% K_2O) of mica. Quartz and feldspars were determined by the pyrosulfate fusion method [KIELY and JACKSON, 1964]. The amorphous material was based on the SiO_2 plus Al_2O_3 dissolved by 0,5 N NaOH treatment, with 10% H_2O added, while kaolinite plus halloysite was based on the difference in Si and Al dissolved by 2,5 min of boiling in 0,5 N NaOH from samples heated for 4 hours at 525 °C and 110 °C [ALEXIADES and JACKSON, 1966]. Chlorite was determined [ALEXIADES and JACKSON, 1966] by measuring the total water of K-saturated samples by ignition loss between 300 to 950 °C, after a deduction of % water loss (300 °C basis) attributable to the other clay minerals present. The vermiculite and montmorillonite contents were derived from cation-exchange capacity (CEC) determinations.

EXPERIMENTS AND CONCLUSIONS

The mineralogical composition of 10 μ fraction of the samples is indicated in Table 1 and Table 2.

The chlorite and amorphous material contents of the samples Makó-1 and Makó-2 are different.

TABLE 1

Minerals present in the core samples from Makó-1 borehole

	Na- FELDSPAR	K- FELDSPAR	QUARTZ	AMORPHOUS MATERIAL	KAOLINITE	MONTMO- RILLONITE	CHLORITE	MICA	TOTAL
I.	2,3	1,0	19,6	7,7	4,6	24,1	11,7	22,1	96,1
II.	3,6	0,8	18,0	7,3	0,0	15,8	18,3	26,9	88,7
III.	2,1	0,5	10,1	9,6	4,9	21,1	12,7	27,3	88,3
IV.	3,6	1,5	22,0	5,2	5,4	20,7	11,8	25,5	95,8
V.	1,9	0,9	20,6	5,9	3,5	12,5	18,4	24,5	88,2
VI.	1,9	1,1	21,0	3,7	3,3	13,8	18,8	24,3	87,9
VII.	4,9	1,2	19,6	9,8	1,7	0,0	22,8	25,6	85,6
VIII.	5,3	2,2	13,8	4,5	2,9	14,2	20,1	28,6	91,6
IX.	3,1	1,8	16,8	2,7	0,9	15,2	20,7	26,2	87,4
X.	4,0	1,3	20,2	2,6	0,0	16,3	27,8	25,3	97,5
XI.	3,9	1,1	11,5	4,7	0,0	8,1	29,9	27,6	86,5
XII.	4,4	0,6	17,4	4,6	1,9	5,8	21,6	26,9	82,2
XIII.	3,2	0,8	19,6	16,2	0,0	1,0	25,4	26,4	82,4
XIV.	3,8	0,4	19,4	9,1	0,0	8,9	18,7	28,8	89,1
XV.	2,3	0,2	13,5	0,6	0,0	19,0	22,0	26,2	83,3
XVI.	6,8	1,3	23,0	1,2	0,3	10,2	24,4	28,2	95,4
XVII.	3,7	0,4	16,9	0,5	0,0	11,1	24,4	31,6	88,6

This difference may be in connection with the time of acid pretreatment carried out to remove carbonates. The time of this pretreatment was longer at the Makó-1 than Makó-2 samples, so one part of chlorite could dissolve, and the amount of amorphous material increased.

The chlorite and mica contents are predominant in the samples of both borings, however, several samples contain considerable amount of montmorillonite. The chemical method used does not give any information whether the montmorillonite is present as a discrete phase or as a component of a mixed-layer structure. According to the previous X-ray investigations the montmorillonite occurs in illite-montmorillonite mixed-layer minerals in these samples [MEZŐSI, 1974]. However, the occurrence of the mixed-layer illite-montmorillonite minerals could be indicated by X-ray diffractometry only in few samples and the quantity determined is also less than by chemical method.

The kaolinite content is small and it disappears at the border of the Upper Pannonian and Lower Pannonian in the Makó-1 drilling but in the Makó-2 drilling kaolinite is present in each determined sample.

The quantity of quartz is similar in both drillings and amounts to about 20%.

Na-feldspar is in larger quantity than K-feldspar but even Na-feldspar is under 10% except in the Miocene psammites and rudites where its quantity is over 10%.

TABLE 2

Minerals present in the core samples from Makó-2 borehole

	Na- FELDSPAR	K- FELDSPAR	QUARTZ	AMORPHOUS- MATERIAL	KAOLINITE	MONTMO- RILLONITE	CHLORITE	MICA	TOTAL
1	3,2	0,7	15,7	3,7	4,6	16,4	33,4	26,0	103,7
2	3,7	0,6	14,9	2,6	4,4	21,5	30,4	28,9	107,0
3	7,6	1,4	13,5	3,6	3,8	17,1	18,1	31,7	96,8
4	5,3	0,4	13,4	2,3	3,6	17,3	25,1	34,6	102,0
5	10,0	4,2	20,1	2,0	0,0	25,6	25,6	20,4	107,9
6	4,9	1,1	17,3	3,0	0,6	8,0	35,4	35,6	105,9
7	7,5	1,4	17,9	3,8	0,7	3,1	34,6	34,6	103,6
8	7,8	2,5	19,6	2,8	0,5	6,1	32,1	32,2	103,6
9	7,6	2,4	15,4	4,9	1,4	16,6	20,2	27,3	95,8
10	6,9	2,1	18,9	1,3	0,9	1,5	38,5	26,8	96,9
11	3,7	2,1	22,5	1,5	3,0	10,5	34,9	27,7	105,9
12	4,2	2,0	21,9	1,4	3,0	10,7	39,0	27,6	109,8
13	4,2	0,9	23,4	1,2	3,0	6,6	42,1	28,5	109,9
14	4,8	1,0	20,1	1,0	2,5	10,4	40,5	28,9	109,1
15	4,8	3,2	23,6	2,7	2,0	12,5	38,5	22,6	109,9
16	2,3	0,5	16,8	1,7	3,2	12,4	45,0	27,4	109,3
17	5,4	2,5	19,9	2,5	2,4	5,4	38,8	25,5	102,4
19	3,4	0,5	18,7	2,8	1,0	8,0	50,8	29,3	109,7
20	4,1	0,2	19,8	2,0	3,1	13,6	33,6	28,3	104,7
21	5,1	0,4	22,1	1,6	0,7	5,0	45,5	28,9	109,3
22	3,9	0,0	18,8	2,2	2,3	11,2	38,2	31,6	108,2
24	2,7	0,0	20,1	2,4	2,7	8,1	32,2	33,3	101,5
25	1,3	0,1	32,8	2,5	1,1	16,4	18,9	36,7	109,8
26	19,6	0,0	12,9	1,9	1,6	22,0	16,5	35,0	109,5
27	12,3	0,4	7,5	2,3	0,7	12,3	41,7	32,1	109,3
28	13,1	0,8	23,6	3,1	0,4	11,6	18,0	25,5	95,1
29	11,6	0,0	28,6	1,6	2,2	12,0	23,2	25,1	104,3
30	12,9	0,6	30,4	2,0	1,2	10,1	19,2	24,4	100,8
31	9,7	0,2	12,8	2,0	1,4	3,1	24,5	35,6	89,3
32	11,0	0,0	15,1	1,9	1,1	2,4	26,1	39,3	95,9

The average values of mineral contents were calculated and listed in Table 3 for the Upper and Lower Pannonian and Miocene samples.

As it can be seen the means in the two drillings are very similar. Means of kaolinite, montmorillonite and amorphous material change in the same way, they are the same in the Lower Pannonian and Miocene samples and they increase in the Upper Pannonian.

The Miocene and Lower Pannonian average values of chlorite are also the same and the chlorite content of Upper Pannonian samples is less.

The mica and Na-feldspar contents increase in order of Upper Pannonian, Lower Pannonian and Miocene. The quantity of quartz changes similarly but the increase is small.

Considering, however, the Miocene pelites and Miocene psammities and rudites, respectively, this sequences may be modified.

Besides the average values the study of the distribution of the minerals with the depth is important because it gives more information on the types of changes than the study only of the means.

The changes of the amounts of the minerals in function of the depth are shown in Fig. 1.

Changes in contents of minerals with the depth are different in the Miocene pelites and Miocene rudites and psammites, similarly to that of the means.

In rudites and psammites the values fluctuate strongly and the tendency of changes differs from changes in the pelitic sediments.

In the Upper and Lower Pannonian samples kaolinite and montmorillonite contents decrease with the depth of burial, chlorite increases and mica increases, too, but less than chlorite. In the Miocene pelites the quantities of montmorillonite and kaolinite are constant, mica increases but chlorite decreases.

The distribution of clay mineral contents is influenced by a great number of factors. Among these the most important ones are the source material, the environment of sedimentation, the distance from the shore and changes during sedimentation and after burial.

TABLE 3

Means of the minerals present in the Upper Pannonian, Lower Pannonian and Miocene samples

		NA-FELDSPAR	K-FELDSPAR	QUARTZ
Makó-1	Upper Pannonian	3,2 (9)	1,2	17,9
	Lower Pannonian	4,0 (8)	7,0	17,7
Makó-2	Upper Pannonian	3,4 (2)	0,6	15,3
	Lower Pannonian	5,8 (14)	1,8	18,9
	Miocene (total)	8,3 (14)	0,4	20,2
	Miocene pelites	4,1 (6)	0,6	19,9
	Miocene rudites	11,4 (8)	0,3	20,4
Means of the	Upper Pannonian	3,2 (11)	1,1	17,4
two borings	Lower Pannonian	5,1 (22)	1,4	18,4
	Miocene (total)	8,3 (14)	0,4	20,2
	Miocene pelites	4,1 (6)	0,6	19,9
	Miocene rudites	11,4 (8)	0,3	20,4

The number of the samples are in bracket.

	AMORPHOUS MATERIAL	KAOLINITE	MONTMORILLONITE	CHLORITE	MICA
	6,2	3,0	15,2	17,2	25,7
	3,3	0,3	10,0	24,3	27,6
	3,1	4,5	18,9	31,9	27,5
	2,4	2,0	10,6	33,5	29,0
	2,2	1,6	10,1	30,4	30,7
	2,2	2,0	8,5	39,8	29,5
	2,1	1,2	11,2	23,5	31,8
	5,6	3,0	15,9	19,9	26,0
	2,7	1,4	10,4	30,2	28,0
	2,2	1,6	10,1	30,4	30,7
	2,2	2,0	8,5	39,8	29,5
	2,1	1,2	11,2	23,5	31,8

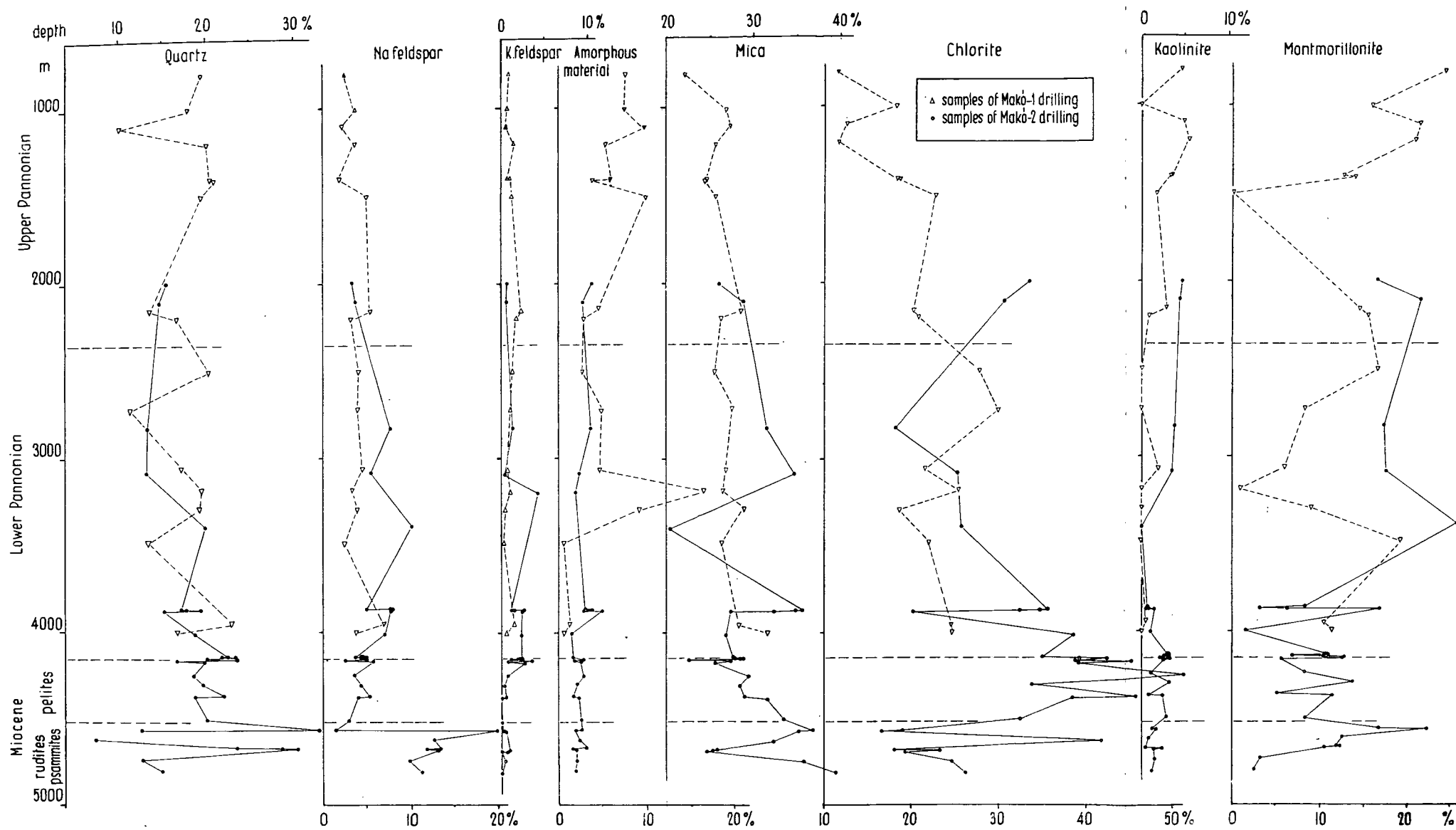


Fig. 1. The amount of minerals in function of the depth

The effect of the individual factors can't be separated, nearly their joint effect can be observed by studying the clay mineral distribution.

The increase of chlorite and mica, the decrease of montmorillonite and kaolinite contents are well known diagenetic changes after burial [GRIM, 1953].

Similar changes in the clay mineral content of the samples investigated suggest diagenetic alterations in this area, too. Decrease in amorphous material with the depth shows the increase of crystallinity which also took place during diagenesis [MURRAY and SAYYAB, 1955].

The distribution of clay mineral content is influenced not only by the diagenesis but by other factors, too. Appearance of the kaolinite in the Miocene may be in connection with the distance from the shore. During sedimentation in the Miocene this part of the "Makó—Hódmezővásárhely trench" had a nearshore position and because of differential flocculation originally more kaolinite could be present [WHITEHOUSE and MCCARTER, 1958] than in the Lower Pannonian when due to the sinking

TABLE 4

Oxidation ratios and $\frac{\text{mica} + \text{chlorite}}{\text{montmorillonite} + \text{kaolinite}}$ (*k*) values of the samples from Makó-2 boring

Samples	Depth	Oxidation ratio		<i>k</i>
		original	fraction of 10 μ	
1	1990,00—1992,40	0,138	0,629	2,82
2	2102,00—2104,60	0,161	0,534	2,29
3	2825,10—2825,20	0,044	0,433	2,38
4	3086,64—3087,80	0,092	0,404	2,85
5	3395,46—3395,58	0,151	*	1,80
6	3870,00—3870,27	0,169	0,423	8,25
7	3872,71—3872,84	0,107	0,339	18,20
8	3873,83—3874,02	0,074	0,433	9,74
9	3875,45—3875,57	0,000	0,312	2,64
10	4014,70—4014,80	0,074	0,495	27,20
11	4140,13—4140,24	0,108	0,275	4,64
12	4145,07—4145,36	0,140	0,244	4,86
13	4145,70—4145,78	0,140	0,259	7,35
14	4146,40—4146,50	0,106	0,294	5,38
15	4152,20—4152,30	0,148	0,280	4,21
16	4156,20—4156,30	0,097	0,313	4,64
17	4162,64—4162,80	0,172	0,518	8,24
18	4176,22—4176,32	0,162	0,336	*
19	4245,25—4245,39	0,178	0,467	8,90
20	4310,70—4301,97	0,127	0,286	3,71
21	4371,02—4371,29	0,121	0,260	13,05
22	4379,45—4379,65	0,116	0,388	5,17
23	4501,48—4501,72	0,045	0,430	*
24	4509,25—4509,65	0,075	0,345	6,06
25	4565,70—4565,84	0,182	0,465	3,18
26	4567,60—4567,71	*	*	2,18
27	4620,35—4620,47	0,289	0,593	5,68
28	4672,30—4673,10	*	0,408	3,65
29	4673,10—4674,60	0,246	*	3,40
30	4674,60—4675,60	*	*	3,86
31	4735,10—4735,22	0,280	0,396	13,35
32	4800,50—4803,60	0,445	0,180	18,68

* There were not enough quantities of samples to carry out these analyses.

of the basin and its filling up with water the place investigated got into the centre of the basin so the quantity of kaolinite decreased.

In Miocene samples quantity of chlorite does not increase with the depth. These samples are more oxidized than it may be expected on the basis of the depth, and therefore diagenetic alterations can be restricted by the environment. The

oxidation ratio $\left[\frac{2 \text{ Fe}_2\text{O}_3}{2 \text{ Fe}_2\text{O}_3 + \text{FeO}} \right]$ of the original samples and of their fraction of 10μ are summarized in Table 4, and the averages of these ratios for the Lower, Upper Pannonian and the Miocene, respectively, in Table 5.

The montmorillonite remains also in the deepest samples. It may be supposed that its transformation to mica was prevented because the available K^+ was not enough for this transformation [WEAVER and BECK, 1971]. The quantity of K-feldspar in these samples is too small to supply enough K^+ .

However, the increase in quantities of chlorite and mica and decrease in montmorillonite and kaolinite with the depth points to a diagenetic alteration, therefore a $\frac{\text{mica} + \text{chlorite}}{\text{montmorillonite} + \text{kaolinite}}$ ratio was calculated. This ratio presumably may be characteristic of diagenetic alteration. (This ratio will be denoted with k .)

TABLE 5

Means of oxidation ratios

	Upper Pannonian	Lower Pannonian	M i o c e n e		
			Total	Pelites	Rudites
Original samples	0,149	0,104	0,189	0,125	0,315
Fraction of 10μ	0,581	0,346	0,378	0,372	0,390

The k values of samples are indicated in Table 4 and Table 6. The mean values of k for the Upper and Lower Pannonian and Miocene, respectively, are shown in Table 7.

Considering the means of this ratio it is found that they increase from Upper Pannonian to Miocene. This increase is only for Miocene pelites but it is not for Miocene rudites and psammites.

The correlation among k values and the types and age of the sediments is shown in Table 8.

In clay marls and aleurites k increases with the age and this increase was not found in sandstones. This fact suggests that diagenetic alterations of clay minerals did not take place at all or these alterations were restricted in the sandstones.

Fig. 2 and Fig. 3 seem to support a genetic connection between mica-chlorite and montmorillonite-kaolinite. Quantities of kaolinite-montmorillonite decrease with the increase of chlorite-mica.

A negativ correlation might be obviously stated between mica-chlorite and montmorillonite-kaolinite and the scattering of the points between the given limits is due to the many factors influencing the genetic connections and, therefore, the distribution of the points.

TABLE 6

Mica + Chlorite
Montmorillonite + Kaolinite (k) ratio of the samples from Makó-1 drilling

Samples	Depth	k
I.	805,30—808,00	1,17
II.	1000,00—1006,00	2,86
III.	1100,50—1102,70	1,53
IV.	1200,00—1206,00	1,42
V.	1403,50—1404,05	2,68
VI.	1404,50—1405,10	2,52
VII.	1500,10—1501,50	28,47
VIII.	2150,00—2150,80	2,84
IX.	2196,00—2196,50	2,91
X.	2500,14—2500,21	3,25
XI.	2722,00—2722,35	7,09
XII.	3064,45—3064,51	6,29
XIII.	3180,15—3180,20	51,80
XIV.	3290,00—3290,20	5,33
XV.	3490,37—3490,42	2,53
XVI.	3951,83—3952,00	5,00
XVII.	4003,20—4004,35	5,04

TABLE 7

Mean values of k for Upper Pannonian, Lower Pannonian and Miocene samples

	Upper Pannonian	Lower Pannonian	M i o c e n e		
			Total	Pelites	Rudites
Makó-1 boring	2,24	4,93			
Makó-2 boring	2,55	4,99	4,91	6,41	3,65
Means of the two borings	2,30 (10)	4,96 (19)	4,91 (12)	6,41 (6)	3,65 (6)

TABLE 8

Mean values of k for the clay marls, aleurites and sandstones

Types of rocks Samples	Clay Marls	Aleurites	Sandstones
Upper Pannonian	1,37	2,67	2,77
Lower Pannonian	5,21	5,89	2,27
Miocene	6,41		
Mean values of each sample	5,20	4,28	2,39

There were not Miocene aleurites and sandstones in these borings.

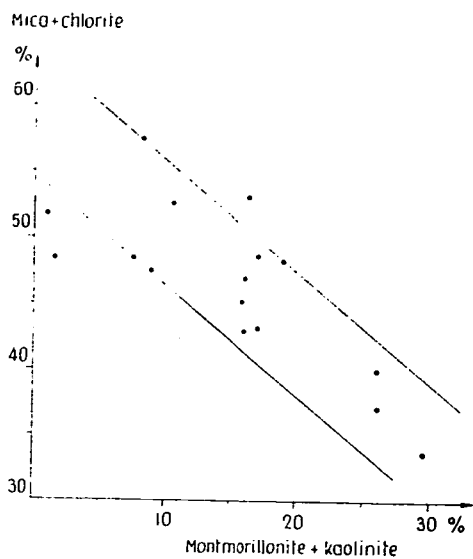


Fig. 2. Connection between mica-chlorite and montmorillonite-kaolinite contents in the samples of Makó-1 boring

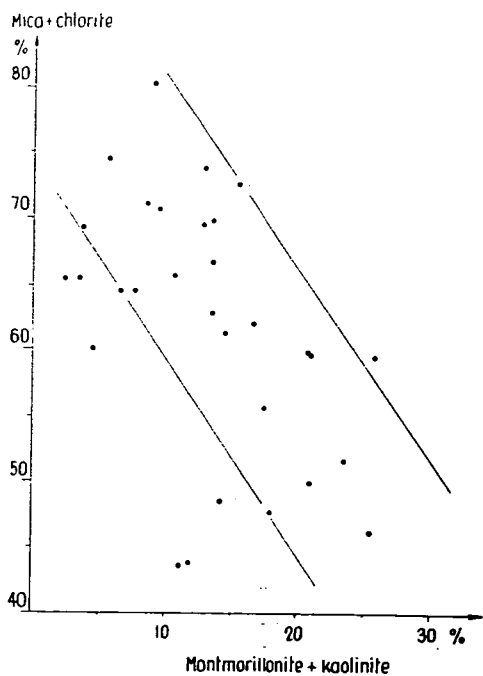


Fig. 3. Connection between mica-chlorite and montmorillonite-kaolinite contents in the samples of Makó-2 boring

Coefficients of regression were calculated on the basis of *k* in function of the depth for the Upper Pannonian, the Lower Pannonian and the Miocene, respectively, and they are listed in Table 9.

TABLE 9

Coefficient of regression and „a” for the Upper Pannonian and the Miocene samples

	Coefficient of regression		„a”	
	Makó-1	Makó-2	Makó-1	Makó-2
Upper Pannonian	$1,77 \cdot 10^{-3}$		0,91	
Lower Pannonian	$0,81 \cdot 10^{-3}$		1,88	– 5,08
Miocene		$2,61 \cdot 10^{-3}$		41,24
Miocene pelites		$- 8,09 \cdot 10^{-3}$		41,24
Miocene rudites		$- 8,06 \cdot 10^{-3}$		– 30,34
		$7,34 \cdot 10^{-3}$		

„a” is the $\frac{\text{mica} + \text{chlorite}}{\text{montmorillonite} + \text{kaolinite}}$ ratio extrapolated on the surface (zero m depth).

These values are positive in the Upper Pannonian and Lower Pannonian samples and negative in the Miocene ones. In the Miocene rudites the coefficient of regression is positive but this value is not to evaluate because its correlation coefficient is only 0,3.

Considering the mean values of *k* for the different substages and epoch mentioned, respectively, it appears that a diagenetic alteration occurred from the Upper Pannonian to the Miocene pelites (Table 7).

This is not keeping with the values of the oxidation ratios, which point to the most oxidized environment in Miocene samples (Table 5) for the oxidized environment is not favourable for diagenetic alterations.

There is no contradiction when not only the mean values of *k* but the coefficients of regression for the Upper Pannonian, Lower Pannonian and the Miocene are taken into account. The positive value of these coefficients suggest the above mentioned diagenetic alteration and the negative value for the Miocene shows restricted changes according to the high oxidation ratio.

Although diagenetic alterations were supposed on the basis of the distribution of the clay mineral contents these alterations can't be considered to be continuous along the depth of burial. If the *k* ratios were extrapolated on the zero meter depth it was found that in some cases these „a” had negative or very high positive values. This fact supports that alterations can't be taken as continuous that is in certain periods of the burial they took place and in other ones they were restricted.

SUMMARY

Core samples from the southern part of the Great Hungarian Plain were studied. Montmorillonite, kaolinite, mica, chlorite, amorphous material, quartz, K-feldspar and Na-feldspar contents were determined in the fraction of 10 μ of samples from Makó-1 and Makó-2 drillings. The quantity of these minerals changes with the depth and age and therefore diagenetic alterations may be supposed.

To characterize the diagenetic alterations a $\frac{\text{mica} + \text{chlorite}}{\text{montmorillonite} + \text{kaolinite}}$ ratio

was calculated. The average of these ratios increases with the age from the Upper Pannonian to the Miocene. The means of the ratios were calculated for the different types of rocks, too. In clay marls and aleurites this ratio increases and in sandstones it remains unchanged from Upper Pannonian to Miocene. Therefore, diagenetic alterations were supposed in clay marls and aleurites but no or restricted alterations in sandstones.

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